

A Study of Contact Resistance of Conductive Adhesives Based on Anhydride-Cured Epoxy Systems

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Abstract—Electrically conductive adhesives (ECAs) are an environmentally friendly alternative to tin/lead (Sn/Pb) solders in electronics packaging applications. However, current conductive technology is still in its infancy and limitations do exist. One of the critical reliability issues is that contact resistance of silver flake-filled ECAs on nonnoble metals increases in elevated temperature and humidity environments. The main objective of this study is to investigate the contact resistance behaviors of a class of conductive adhesives, which are based on anhydride-cured epoxy systems. Curing profiles, moisture pickup, and shifts of contact resistance of the ECAs on a nonnoble metal, tin/lead (Sn/Pb), during aging are investigated. Also, two corrosion inhibitors are employed to stabilize the contact resistance. The effects of these corrosion inhibitors on contact resistance are compared. It is found that: 1) this class of ECAs shows low moisture absorption, 2) the contact resistance of the ECAs on Sn/Pb decreases first and then increases slowly during 85 °C/85% relative humidity (RH) aging, 3) one of corrosion inhibitors is very effective to stabilize contact resistance of these ECAs on Sn/Pb, and 4) the corrosion inhibitor stabilizes contact resistance through adsorption on Sn/Pb surfaces. From this study, it can be concluded that ECAs based on anhydride cured epoxy systems are promising formulations for electronics packaging applications.

Index Terms—Anhydride, contact resistance, corrosion inhibitor, electrically conductive adhesives, electronics packaging, epoxy.

I. INTRODUCTION

ELECTRICALLY conductive adhesives (ECAs) are generally composed of an insulating adhesive resin and highly conductive fillers [1]–[6]. Epoxy resins are the most commonly used polymeric resins in ECAs because they have superior overall properties. Silver (Ag) flakes are generally used as the conductive fillers in ECA formulations because Ag has high electrical conductivity. The properties of the composites are understood in terms of percolation phenomena; when a sufficient amount of the conductive filler is loaded into the insulating resin, the composite transforms from an insulator to a conductor, the result of continuous linkage of filler particles. This is shown graphically in Fig. 1. As the volume fraction of

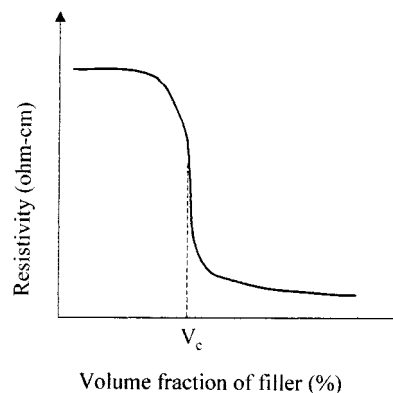


Fig. 1. Resistivity change with filler concentrations.

the filler is increased to a critical value (V_c), resistivity of the composite drops sharply. Beyond this critical volume fraction, conductivity only changes slowly [7], [8]. For silver flakes, the critical concentration is from 25–30 vol%.

As a potential tin/lead solder replacement in electronics packaging, ECAs are environmentally friendly and offer many advantages including mild processing condition and better thermomechanical performance [1], [5], [6]. Compared to mature soldering technology, ECA technology is still in its infancy and thus has many reliability issues. One critical reliability issue is that most of the commercial Ag flake-filled ECAs, when placed on nonnoble metal and exposed to high temperature and humidity, show dramatic increase in contact resistance [9]–[13]. Our previous study indicated that a metal oxide layer caused by galvanic corrosion of the nonnoble metal at the interface was the main reason for the contact resistance shift [14]. Based on this understanding, ECAs with stable contact resistance on nonnoble metals are being developed in our laboratory. One of the approaches of developing ECAs with stable contact resistance is to select proper polymeric resin formulations. Another approach to stabilize contact resistance is to use corrosion inhibitors [15]. In this study, resin formulations consisting of epoxy and anhydrides were used to formulate ECAs. The overall properties, especially contact resistance shift, of these ECAs were investigated. Also, effects of corrosion inhibitors on contact resistance were studied.

II. EXPERIMENTAL

A. Materials

The epoxy resin used was Epon 862, which is based on diglycidyl ether of bisphenol-F (DGEF), and was supplied by Shell

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Chemical Company. The epoxy equivalent weight (EEW) of this epoxy resin was approximately 170 g/equivalent. Three anhydrides, methylhexahydrophthalic anhydride (MHHPA), hexahydrophthalic anhydride (HHPA), and, 4-methylphthalic anhydride (MPA) were used as curing agents (or hardeners) and obtained from Aldrich Chemical Company. 2-Ethyl-4-methylimidazole (2E4MZ), employed as the catalyst, and two corrosion inhibitors were also purchased from Aldrich Chemical Company.

An adhesion promoter, A-180, was supplied by OSI Specialties. All the chemicals were used as received. A silver flake, 26LV, was purchased from Degussa Corporation.

B. Preparation of ECAs

1) *Formulation of Resins:* The resins for the ECAs were formulated based on the following procedure:

- a curing agent was added in an appropriate quantity to a known amount of the epoxy resin (the equivalent ratio of anhydride to epoxide was kept at 0.85);
- the mixture was stirred with heat, if necessary, until a homogeneous solution was formed;
- after the solution cooled down to room temperature, a certain amount of 2E4MZ (catalyst level was 0.5 parts per hundred parts of total resin) and a corrosion inhibitor (inhibitor concentration was 5 parts per hundred parts of total resin) were added and mixed thoroughly.

2) *Formulation of ECAs:* A certain amount of the Ag flake was added to a known amount of the resin formulated in the above section. The filler concentration of the all the ECAs was kept at 80 weight%. The mixture was pre-mixed using wood sticks and then was thoroughly mixed using a three-roll mill until a homogeneous paste was formed.

C. Curing Behavior

The curing behavior of these ECAs was determined using a differential scanning calorimeter (DSC) from TA Instruments, model 2970. Dynamic scans were made on samples of appropriate weight, generally 20 mg, at a heating rate of 5 °C/min, usually from 25–300 °C. The samples were placed in hermetic aluminum DSC pans and scanned in a nitrogen purge gas. After the dynamic scan, the sample was cooled to room temperature and then scanned again under a modulated mode at the same heating rate from 25–250 °C. Glass transition temperature (T_g) of the cured sample was derived from the curve of reversible heat flow versus temperature.

D. Study of Moisture Absorption

Moisture absorption of the resin of an ECA was measured by monitoring the mass changes of the cured resin with time in a chamber, model CEO932W-4 from Lunaire Environmental, under 85 °C/85%RH. The samples were prepared by curing approximately the same volume of each resin in an aluminum pan with a 3-cm diameter. After cured and removed from the pan, the samples were placed in the chamber and their mass changes with time were recorded. Three specimens were tested for each sample. The average of moisture absorption of the three specimens was reported.

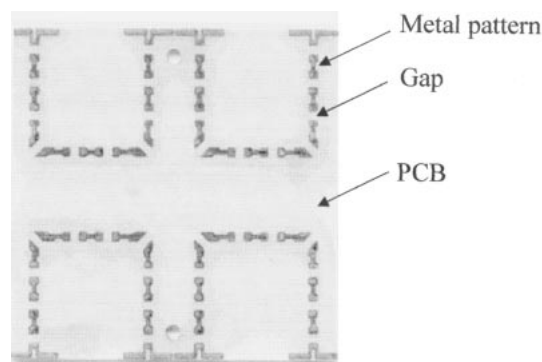


Fig. 2. Contact resistance test device.

E. Study of Contact Resistance Shifts

Shifts of contact resistance between an ECA and a metal were tested using the test device shown in Fig. 2. In the test devices, metal patterns were deposited on a piece of FR-4 board. An ECA paste was dispensed on the gaps. After curing, the total resistance of the circuit was measured using a Keithley multimeter, model 2000, with a four-point probe. Three specimens were prepared and tested for each sample. The specimens were aged in the temperature and humidity chamber under the aging condition of 85 °C/85%RH. The resistance was measured periodically. The average of the results of the three specimens was reported.

F. Adsorption Study

Adsorption of a corrosion inhibitor on Sn/Pb surface was studied using following procedure: a) prepared an aqueous solution of an inhibitor with a concentration of 3×10^{-5} g/ml; b) mixed 2 g of a Sn/Pb powder with 8 ml of the inhibitor solution and kept the mixture at room temperature for 24 h; c) determined the concentration of the inhibitor in the solution of the mixture and compared with that of the original solution.

The concentration of an inhibitor in a solution was determined based on the absorbance at a predetermined wavelength using a UV visible spectrometer, model DU 520, from Beckman. The inhibitor solution was scanned from wavelength 190–400 nm first. The wavelength at which the inhibitor showed the highest absorbance was used to determine the concentrations of the inhibitor in the original solution and the solution of the mixture.

III. RESULTS AND DISCUSSION

A. ECA Formulations

Three ECAs, ECA-1, ECA-2, and ECA-3, were formulated with the epoxy resin (Epon 862) and the anhydrides, HHPA, MHHPA, and MPA, respectively. Heat was applied when the epoxy resin was mixed with HHPA and MPA because both ingredients were solids at room temperature. After the mixtures were cooled down to room temperature, HHPA was still in the liquid state in the mixture. However, it was noted that MPA crystallized into very fine powders evenly dispersed in the epoxy resin. As a result, ECA-1 and ECA-2 had lower viscosity than ECA-3 at room temperature.

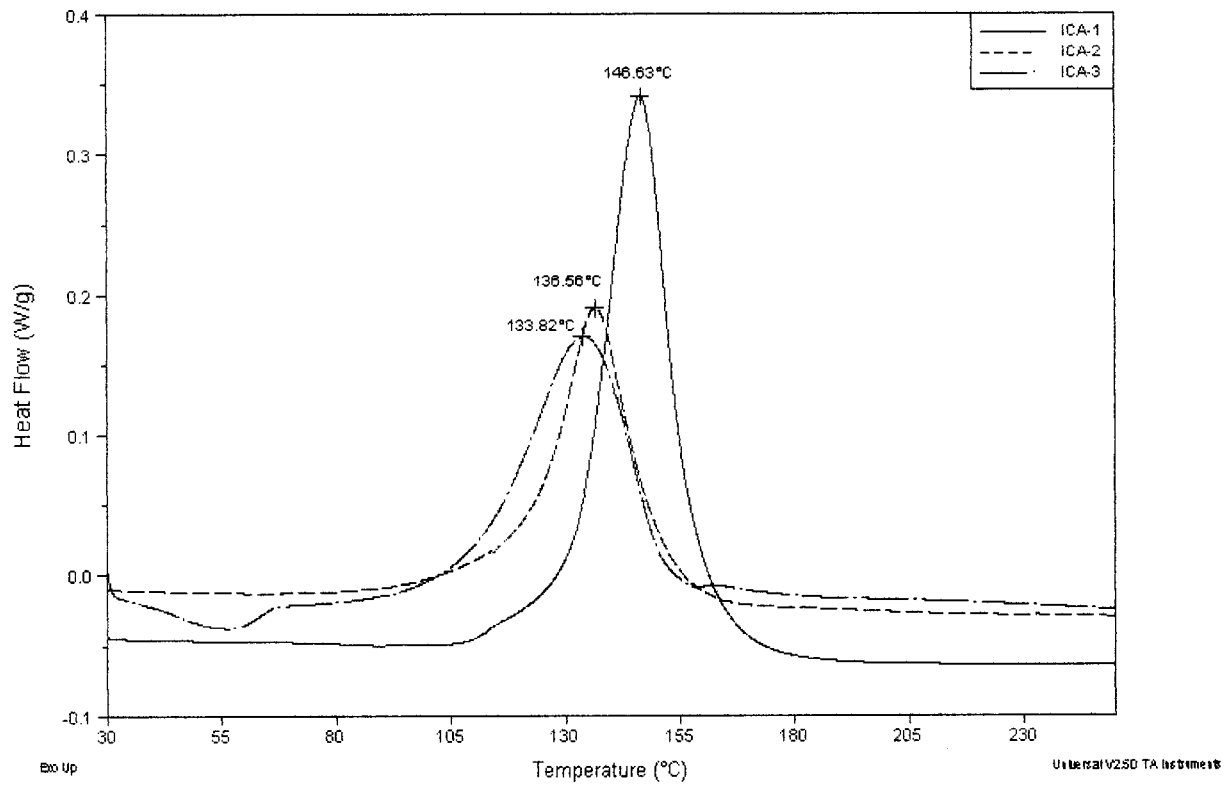


Fig. 3. Heat flow versus temperature of three ECAs.

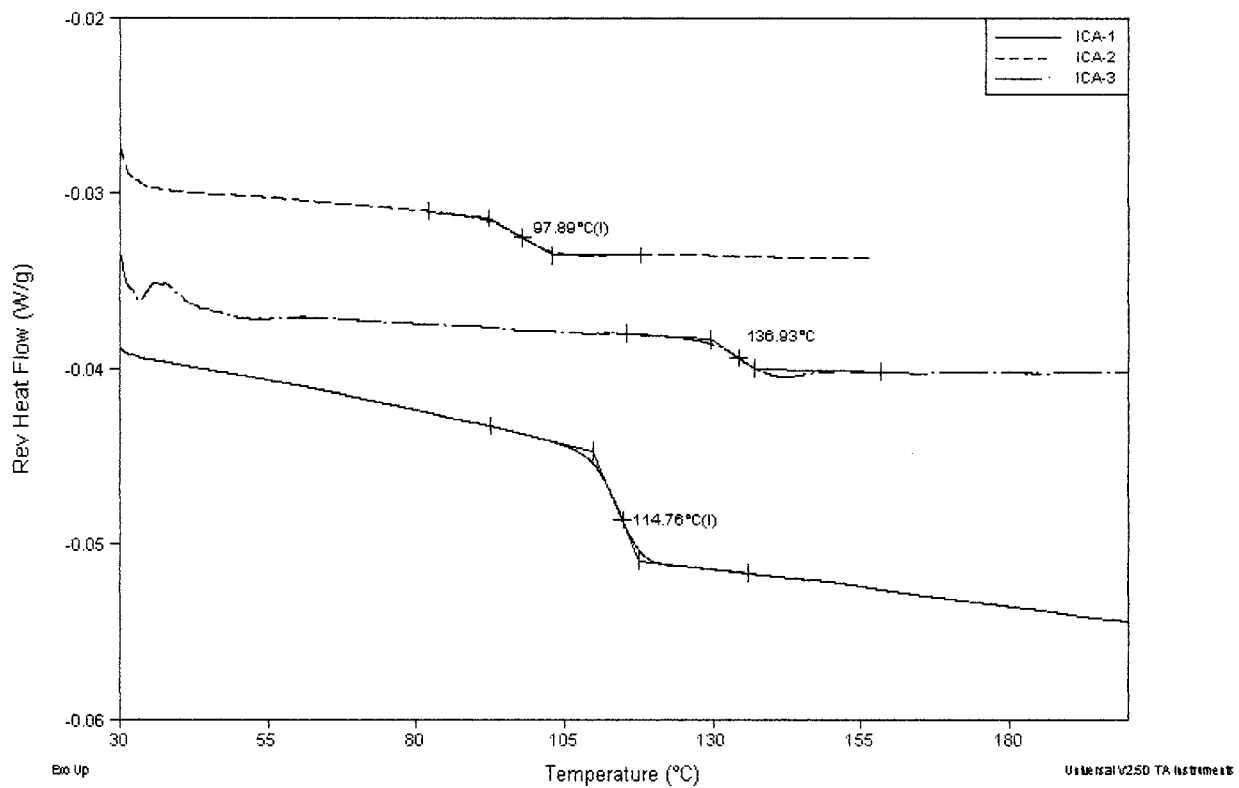


Fig. 4. Reversible heat flow versus temperature of three ECAs (glass transition temperatures were labeled).

B. Curing Behavior

Cure behavior of these ECAs and the glass transition temperatures (T_g) of the cured ECAs were studied by differential scan-

ning calorimetry (DSC). The curing profiles of the ECAs are shown in Fig. 3 and T_{gs} of the cured ICAs are shown in Fig. 4. All of the three anhydrides cured the epoxy within narrow tem-

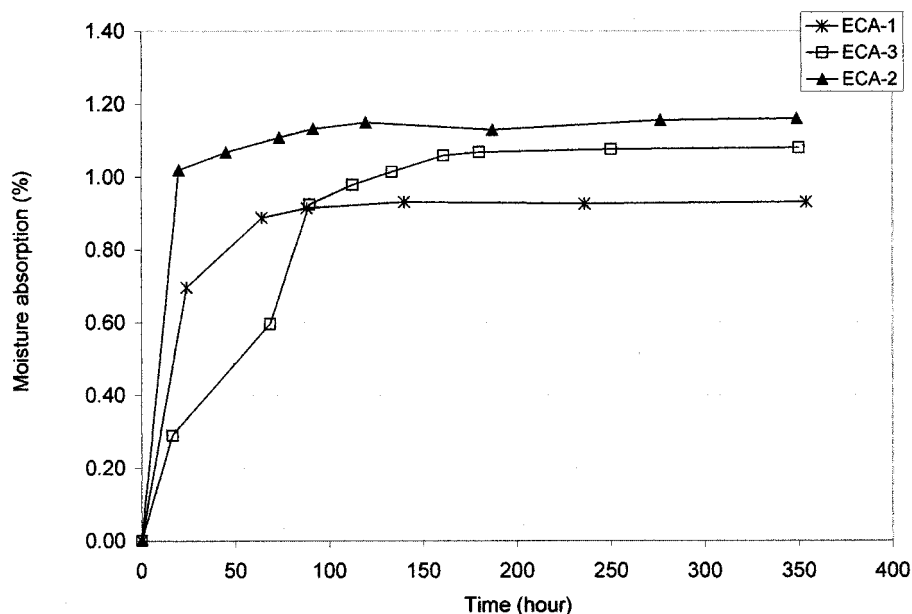


Fig. 5. Moisture absorption of the cured resins of the ECAs.

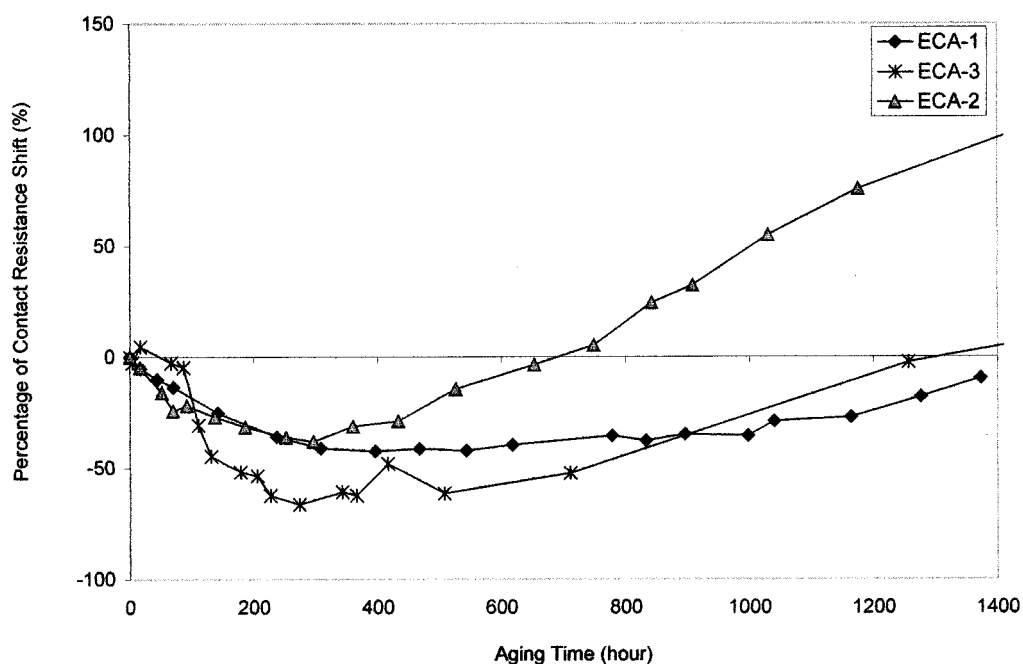


Fig. 6. Shifts of contact resistance of ECAs on Sn/Pb.

perature ranges. But HHPA cured the epoxy at a higher temperature range (cure peak at a higher temperature range). All three anhydrides provided the resin with high T_g s, which was desirable for a reliable ECA. The MPA cured epoxy showed the highest T_g (136.9 °C) and MHPA cured epoxy showed the lowest T_g (97.9 °C). In the later studies, the formulated ECAs were cured at 150 °C for 30 min.

C. Moisture Absorption

Our previous study proved that metal oxide formation caused by galvanic corrosion of the nonnoble metal at the interface was responsible for the contact resistance increase [14]. Galvanic

corrosion happens only under wet conditions with the presence of an electrolyte solution. Moisture absorbed by the cured ECA diffuses into the interface between the ECA and the nonnoble metal and forms an electrolyte solution. Galvanic corrosion does not occur without the electrolyte solution. Therefore, in order to stabilize contact resistance, it is essential to lower the moisture absorption of the cured ECAs. Moisture absorption of these three cured formulations is given in Fig. 5. As can be seen from the figure, all of them showed low moisture absorption, lower than 1.2%. Among them, HHPA cured epoxy showed the lowest moisture absorption, lower than 1.0%. Therefore, these formulations showed the potential of improving contact resistance stability.

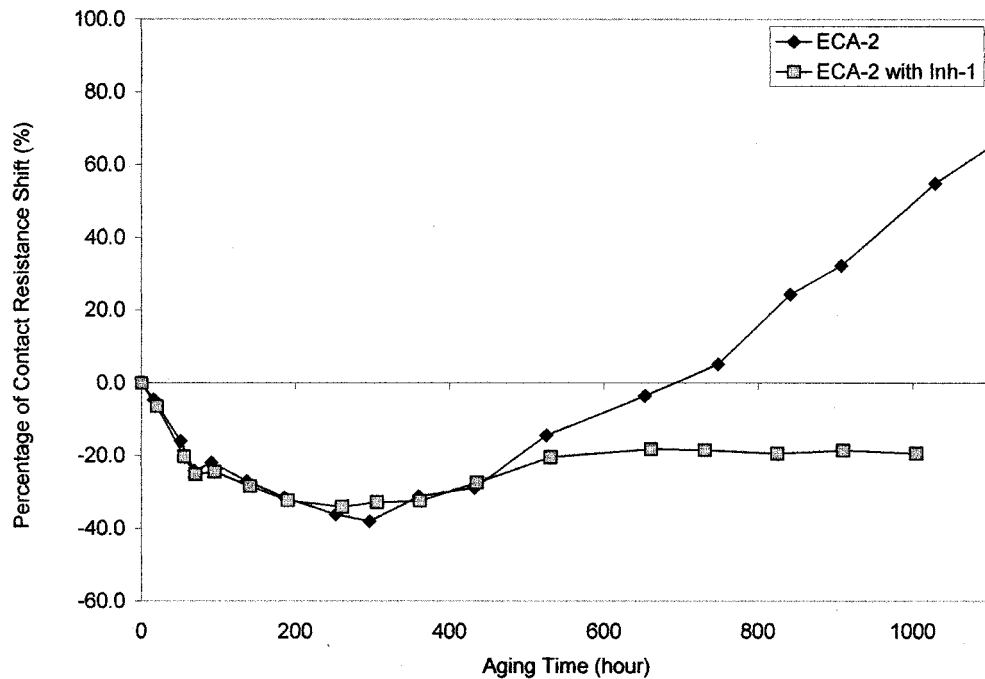


Fig. 7. Shifts of contact resistance of ECA-2 with and without a corrosion inhibitor (inh-1).

TABLE I
ABSORBANCE OF Inh-1 AND Inh-2 SOLUTIONS

	Inh-1 solution (at 235 nm)		Inh-2 solution (at 263 nm)	
	Before mixed with Sn/Pb powder	After mixed with Sn/Pb powder	Before mixed with Sn/Pb powder	After mixed with Sn/Pb powder
1	3.586	0.846	3.488	3.294
2	3.556	0.851	3.399	3.285
3	3.575	0.860	3.442	3.296
Average absorbance	3.572	0.852	3.443	3.291

D. Contact Resistance Shift

Contact resistance shifts of each of the formulated ECAs on Sn/Pb metal were tested. Resistance changes with aging time for ECA-1, ECA-2, and ECA-3 are shown in Fig. 6. Based on the criterion set by National Center of Manufacturing Science (NCMS), contact resistance shift of a desirable solder replacement ECA should be less than 20% after 500-h 85 °C/85%RH aging [11].

According to results from above Fig. 6, it can be seen that all three ECAs showed the similar trend of contact resistance change during aging. The contact resistance on Sn/Pb decreases slightly at the beginning and then increased with further aging. The ECA-1 showed slowest contact resistance increase. The slight decrease in the early stage of aging was

probably due to the fluxing action of the organic acid which was formed after the residual anhydride was hydrolyzed by moisture [16]. The contact resistance increase after the initial decrease was probably due to the metal oxide formation caused by galvanic corrosion of Sn/Pb metal after moisture penetrated into cured polymeric matrix and condensed at the interface between the ECA and Sn/Pb metal surface. ECA-1 had the lowest moisture absorption and it also showed the slowest contact resistance increase. These results were consistent with galvanic corrosion mechanism. Due to the lower moisture absorption of ECA-1, the rate of galvanic corrosion at interface between ECA-1 and Sn/Pb was slower and thus contact resistance increased slower. From this study, it can be concluded that the HHPA-cured ECA, ECA-1, was more

desirable than the other two ECAs in terms of contact resistance stability.

E. Effects of Corrosion Inhibitors

Galvanic corrosion has been identified as the main mechanism for the unstable resistance phenomenon. Therefore, one of the approaches to stabilize contact resistance was to use corrosion inhibitors to slow down the rate of corrosion [15].

ECA-2 was selected in this study because it showed fastest contact resistance increase. Two corrosion inhibitors (Inh-1 and Inh-2) were added into ECA-2 formulation at the concentration level of 5 parts of the inhibitor per hundred parts of the resin of the ECA. The contact resistance shifts of the ECA-2 with the corrosion inhibitors during aging were measured and compared to that of ECA-2 without any corrosion inhibitors. The results indicated that Inh-2 was not effective but Inh-1 was very effective to stabilize contact resistance of the ECA on Sn/Pb. Therefore, only the contact resistance shift of ECA-2 with Inh-1 is shown in Fig. 7. From Fig. 7, it can be seen that the ECA-2 with inh-1 showed stable contact resistance after the initial decrease than the ECA-2 without any corrosion inhibitors.

F. Study of Effectiveness of Corrosion Inhibitors

The general mechanism for organic corrosion inhibitors is to adsorb on metal surface and separate metal from corrosive environments [17]. Therefore, adsorption ability of a inhibitor on a metal is related to the effectiveness of the inhibitor to hinder corrosion.

Solutions of Inh-1 and Inh-2 before and after mixed with a Sn/Pb powder were studied using UV-visible spectrometry at wavelengths of 235 nm and 263 nm, respectively. The absorbance of these solutions were measured and compared. Three measurements were taken for each sample. The absorbance results are shown in Table I. As can be seen from the Table, the absorbance of Inh-1 solution after mixed with Sn/Pb decreased significantly but the absorbances of Inh-2 solutions before and after mixed with Sn/Pb powder were similar. These results strongly indicated that the Inh-1 adsorbed on the Sn/Pb surfaces after mixing. Due to its strong adsorption on Sn/Pb surface, Inh-1 was much more effective to stabilize contact resistance of ECAs on Sn/Pb surfaces.

IV. CONCLUSIONS

All three anhydrides cured the epoxy resin within narrow temperature ranges. MPA cured ECA had the highest T_g and MHHPA cured ECA had the lowest T_g . Anhydride-cured epoxy systems showed low moisture absorption. Among the anhydrides tested, HHPA provided the system with the lowest moisture absorption. Contact resistance of the ECAs based on the anhydride-cured epoxy systems Sn/Pb surfaces decreased initially and then increased gradually during the elevated temperature and humidity aging. HHPA cured ECA, ECA-1, showed high potential as solder replacement materials because it had the slowest increase of contact resistance during aging.

One corrosion inhibitor, Inh-1, was very effective to stabilize contact resistance of the ECAs on Sn/Pb and it stabilized contact resistance by its strong adsorption on Sn/Pb surfaces.

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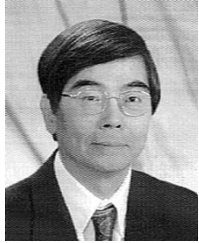


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